

RAPID, MEASUREMENT-BASED SOURCE APPORTIONMENT OF AIR PARTICULATE MATTER

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INTRODUCTION

There are two basic approaches to the quantitative apportionment of air particulate matter (PM) source contributions at a given receptor site and point in time. The first approach is based on a detailed inventory of the contributing local and long range sources and their expected PM emission activities (at the selected point in time minus the calculated transport time), combined with the use of atmospheric dispersion models capable of calculating the probability that particulate matter emitted by a given source will be transported to the selected receptor site at that particular point in time. The second approach is based on detailed physical and chemical characterization of one or more PM samples collected at the selected receptor site and time point, combined with the use of quantitative receptor models capable of apportioning these characteristics to potential local and long range sources with the aid of a library of known source patterns.

As pointed out in many textbooks [1], both approaches should be combined whenever feasible. In practice, however, most PM source apportionment efforts cannot draw upon reliable source emission and activity inventories and are also severely constrained by the high cost and time requirements of comprehensive PM characterization efforts. As a result, our present knowledge about the relative contributions of local and long range PM sources to air quality problems within many North American airsheds, let alone airsheds in other areas of the world, provides an inadequate basis for effective regulatory measures aimed at cost-effective protection of health and environment. Consequently, there is a need for the development of rapid, reliable and cost-effective PM characterization and apportionment techniques.

Currently used characterization methods for PM receptor samples are typically based upon inorganic analysis of 24-hr filter samples by means of x-ray fluorescence (XRF), proton-induced x-ray emission (PIXE), scanning electron microscopy with energy dispersive x-ray analysis (SEM-EDAX), or neutron activation analysis (NAA) methods. Over the past decade organic PM characterization methods involving solvent extraction of 24-hr filter samples followed by combined gas chromatography and mass spectrometry (SX-GC/MS) have demonstrated their power in providing hundreds of potential source marker compounds, particularly for a wide range of petroleum- and biomass-type materials combustion and processing sources which fail to produce characteristic inorganic markers or patterns. Quantitation of organic as well as inorganic measurements is typically achieved on the basis of mass balance techniques involving careful weighing of moisture-equilibrated filters (before and after exposure) and expressing chemical parameters in percentage of total sample mass.

Over the past few years, the advantages of novel PM sampling and analysis methods requiring only 1- to 2-hr long sampling periods, thereby producing time-resolved circadian PM profiles revealing characteristic anthropogenic activity and/or meteorology cycles as well as episodic events, were demonstrated for selected organic PM marker components by some of the present authors [2] using thermal desorption (TD) GC/MS techniques. Equally fast sampling approaches to inorganic PM characterization by means of SEM-EDAX and PIXE were demonstrated by Anderson et al. [3]. Although use of these novel, rapid sampling methods can greatly speed up source attribution, quantitative source apportionment still requires laborious filter weighing operations. Moreover, in areas with new or unusual sources and fuels, existing source profiles are often inadequate, thus requiring lengthy, costly and socio-politically sensitive source sampling and characterization operations.

A novel, rapid PM characterization strategy is presented. The procedures outlined can drastically reduce the time and effort required for exploratory source apportionment studies and are based on a combination of: (1) rapid TD-GC/MS of 2-hr PM samples; (2) differential source plume profiling of complex sources or source clusters; and (3) real-time, size-distributed particle concentration measurements.

EXPERIMENTAL

PM samples for TD-GC/MS analysis were collected on 19 mm dia. quartz fiber (QF) filters in a 16.7 l/min flow of air passing through an isokinetic (dichotomous sampler type) ambient air sampling tower equipped with a 10 micrometer cut-off impactor. QF filters were cleaned by preheating in a high temperature furnace and stored in particle-free containers, as described by Sheya et al. [4]. QF slivers of approximately 2 mm wide were reproducibly cut from the particle-laden filters and inserted into carefully cleaned borosilicate glass sample tubes and quickly inserted in to the hot (250 C) injection port of a GC system (HP 5890A) equipped with a 10 m long, 320 micrometer i.d. GC column coated with an 0.25 micrometer layer of DB1 and connected to a desk-top quadrupole mass spectrometer (HP MSD5972). When rapid heating of the QF slivers to higher temperatures is desired, e.g. for pyrolysis studies, the pyrex tubes can be lined with ferromagnetic foils of precisely known inductive heating behavior and a well-defined end point temperature corresponding to the Curie-point temperature of the selected alloy.

GC/MS data were analyzed using the IIP ChemStation program and NBS mass spectral library. Multivariate statistical analysis of relative peak intensity data, as well as the corresponding size-distributed particle count and meteorology data where applicable, was performed by means of principal component analysis (PCA) using the NCSS version 7.0 software package, followed by Varimax rotation of the PCA loadings and scores to highlight the more highly orthogonalized components in PCA space. Where appropriate, the scores of the first four Varimax factors were plotted in the form of time-resolved "skyline" plots using standard plot programs.

Size-distributed particle concentration measurements were performed with a Climet Model CI 208C 8-channel particle analyzer with specially built computer interface. Total particle volumes in each size range were calculated assuming distribution-corrected average particle sizes and spherical particle shapes.

RESULTS AND DISCUSSION

Figure 1 shows the close agreement between TD-GC/MS and SX-GC/MS analysis profiles of PM samples obtained from the same Hi-Vol quartz fiber filter. In studies currently underway in our laboratory of the nearly 100 compound peaks routinely monitored in the GC/MS profiles approximately 90 % are readily identifiable in both profiles, with the intensities of most of these showing strong correlations. Clear differences are seen in the broad multimodal "humps" underlying both profiles. These humps, generally referred to as the unresolved complex matter (UCM), are highly characteristic of the GC/MS profiles of both solvent and thermal extracts from PM receptor samples and are also seen in most combustion source samples. Apparently, the physicochemical differences between both extraction methods result in somewhat different relative UCM fraction yields. Presumably, for the SX-GC/MS method these relative UCM fraction yields will also be affected by the choice of the solvent whereas the relative UCM yields of the TD-GC/MS technique may well vary as a function of desorption conditions. Thus far, the observed differences appear to be quantitative rather than qualitative and, thus, should be amenable to routine standardization and calibration procedures.

The type of information obtainable from time-resolved circadian TD-GC/MS profiles is illustrated by the skyline plots shown in figure 2. Rather than to show an arbitrary selection of the many different single compound profiles produced by this technique each skyline plot in figure 2 shows a linear combination ("factor") of highly correlated compound profiles, thought to represent a particular PM 10 source, or combination of related sources. To further illustrate the validity of the factor analysis approach to source detection, also commonly used to reduce and interpret inorganic PM10 compound data [5], the same type of factor loading patterns producing the factor score profiles shown in figure 2 (representing a series of PM10 samples collected at the international bridge in Hidalgo, at the USA/Mexico border in December 1995) was found in two other sets of samples obtained at the border in different locations and at different time periods in December. As expected, combustion sources known to produce significant organic PM emissions are dominant. However, the prominent (5 sigma) "urban dust" event observed in the evening of December 6th is largely characterized by inorganic, re-entrained city dust components but can still be observed thanks to several characteristic organic markers [6].

Since weighing of 2-hr filter samples would not only be very time-consuming but is also impractical in view of the more than 10x lower average sample quantities (compared to conventional 24-hr samples), a different approach needs to be found to calibrate each sample with regard to differences in sample size as a basis for quantitative compound analysis by TD-GC/MS. This is achieved by the use of multichannel (size-distributed) particle counting in parallel with the collection of each 2-hr filter sample, thus allowing us to calculate the number of particles collected by the filter in each size category. As shown in figure 3, the four upper and the four lower channels of an 8-channel optical particle counter (OPC) track each other closely with regard to relative changes in calculated total particle counts. Between these two sets of channels, however, significant quantitative as well as qualitative differences can be observed. On several occasions we have been able to correlate calculated total particle volumes (assuming spherical particle shapes for the purpose of convenience) with PM mass measurement data obtained with nearby situated Beta-gauge instruments. An example of the close agreement achievable using a simple, single shape plus density correction coefficient is shown in figure 4. Both weighing and size-distributed counting techniques have their potential strengths and weaknesses as book-keeping ("balancing") methods for PM samples and their components, as non-correctable losses and gains in particle numbers as well as in total particle mass can occur on the filter during and after collection. A detailed discussion of these pros and cons falls outside the page limitations of these preprints but some relevant data will be presented in the talk. It should be noted that each particle size-distribution profile is a vector unto itself. Consequently, substitution of particle count vectors for mass numbers in source apportionment methods such as the widely used chemical mass balance (CMB) model, requires some adaptation of the algorithms to higher dimensional outputs, e.g. by substituting partial least squares or canonical correlation analysis methods for the conventional multilinear regression method.

Finally, we need to examine the possibility of by-passing the conventional source sampling and characterization methods, requiring the use of elaborate equilibrium chambers permitting direct stack, flue or tailpipe sampling of individual sources. Although these methods are likely to remain indispensable for large comprehensive source characterization studies, conceptually the main difference with ambient source plume samples taken in close proximity to the source is the inevitable dilution with ambient air containing background PM. However, more than likely the source is using plenty of intake air with background PM (which may or may not be altered during its passage). This intake air background can usually be ignored in the source profile because of the very high concentrations of emitted particulates. However, these high concentrations, often accompanied by above ambient temperatures and particle flow velocities, come at a high cost since the concentration, size distribution and composition of the sampled particles may be affected by various non-equilibrium processes.

When obtaining ambient plume samples in close proximity to the source the advantages of more highly representative particle equilibria are now being traded off for the disadvantages of higher dilution and additional contamination with background PM. Thus, it will largely depend on the sensitivity and specificity of the analytical methods used to obtain the needed PM source profiles whether this trade-off is acceptable or not. As shown by the factor analysis examples in figure 2 the large numbers of highly specific variables in GC/MS based methods enables successful linear deconvolution of complex mixture profiles into their chemical components. Based on hands-on experience we expect relatively few problems in subtracting background contributions from targeted source profiles as soon as the contribution of the targeted source, or source cluster, accounts for more than 20-30 % of the total PM signal.

In order to verify both the ambient equilibrium conditions of the source PM components, the nature and concentration of background PM components and the rate of dilution it will be advantageous to obtain control samples and size-distributed particle count measurements directly upwind of the source (or source cluster) as well as further downwind inside the plume. Of course, the proposed approach will not work well with source (cluster) plumes which are too high above ground to be sampled conveniently at a reasonable distance from the source (cluster) and will also be strongly dependent upon favorable weather conditions.

Figure 5 provides a purely conceptual example of the combined use of differential source plume profiling and size-distributed particle volume balancing as a way of determining the quantitative relationship between the intensities of observed chemical source markers (or marker pattern) in receptor samples and the volume fraction of collected particulate matter explained by the source or source cluster to which the marker(s) or pattern can be attributed.

CONCLUSIONS

Direct TD-GC/MS analysis of 1- to 2-hr QF filter samples provides a rapid approach to characterization and identification of organic PM components in receptor as well as source samples.

Size-distributed particle concentration measurements, obtained in parallel with PM filter sampling, are presented as an in-situ, real-time calibration alternative to conventional filter weighing procedures.

Differential profiling of ambient source plume samples, in conjunction with size-distributed particle concentration measurement, is proposed as a low cost, minimally intrusive method of obtaining characteristic PM emission profiles of complex or inaccessible sources or source clusters.

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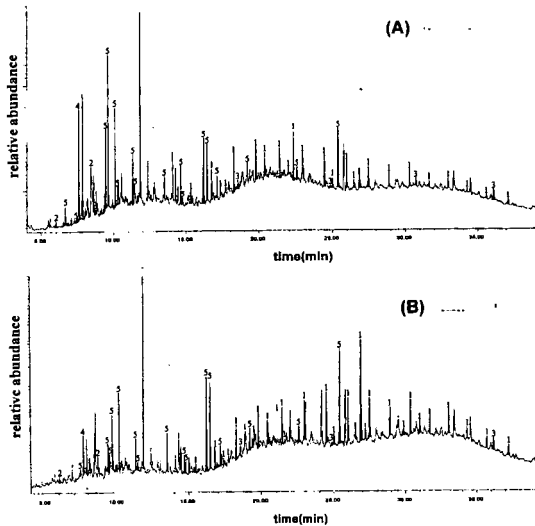


Figure 1. Comparison of solvent extracted (A) and thermally extracted (B) PM constituents. Peak labels: (1) alkanes; (2) N-containing compounds; (3) aromatics and PAH; (4) aliphatic alcohols and phenols; and (5) other O-containing compounds.

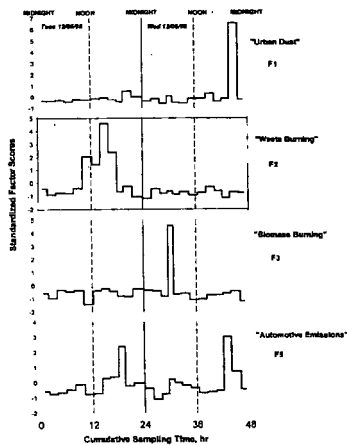


Figure 2. Time-resolved plot of four Varimax-rotated factor scores for the Hidalgo (TX) PM data set. All interpretations are tentative until confirmed by area-specific source sampling. Since factor scores are standardized a score of "3" can be regarded as a "3 σ event" in statistical terms, and so on. Note the characteristic periodic traffic peak pattern of F5 events and, the episodic character of major F1 and F2 events.

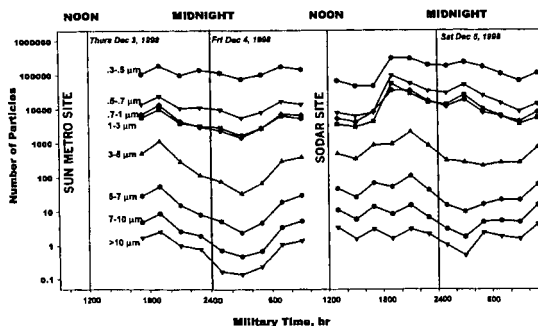


Figure 3. Averaged (2-hr averages of 4 min. intervals) 8-channel particle count at 2 El Paso (TX) sites. Note the "natural" division between the lower and higher size classes.

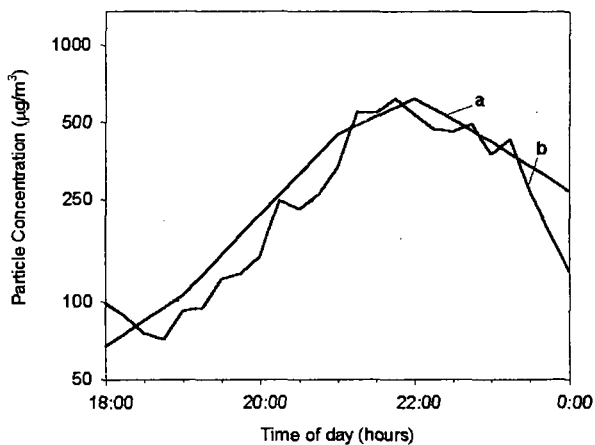
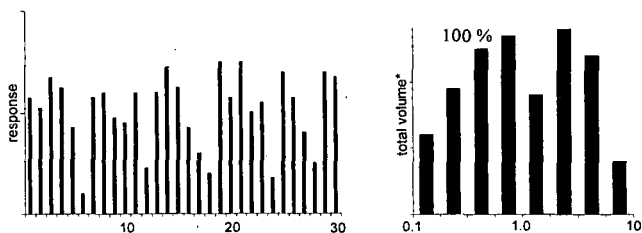


Figure 4. Use of beta attenuation monitor particle density measurements to calibrate particle density values calculated from multichannel particle count data at the Calexico site in December 1992.

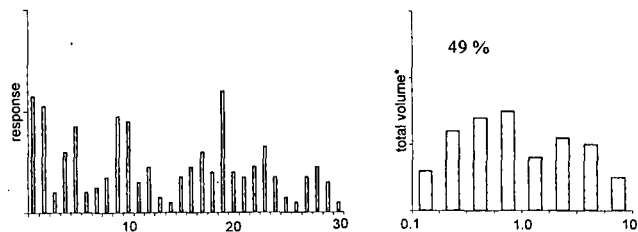
A. SOURCE PROXIMITY GRADIENT PROFILES (downwind)

c.g. Spectroscopic Data

Size / Volume Data



B. AMBIENT BACKGROUND PROFILES (upwind)



C. BACKGROUND-SUBTRACTED SOURCE PROFILES (A minus B)

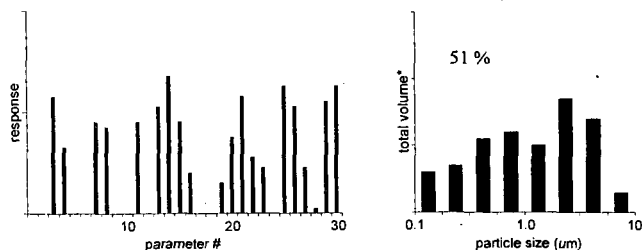


Figure 5. Conceptual illustration of the proposed Differential Source sampling approach aimed at producing characteristic, background-subtracted source profiles and the accompanying size-distributed particle data.